Epitaxial thin films of the giant-dielectric-constant material $CaCu_3Ti_4O_{12}$ grown by pulsed-laser deposition

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Pulsed-laser deposition has been used to grow epitaxial thin films of the giant-dielectric-constant material $CaCu_3Ti_4O_{12}$ on $LaAlO_3$ and $SrTiO_3$ substrates with or without various conducting buffer layers. The latter include $YBa_2Cu_3O_7$, $La_{1.85}Sr_{0.15}CuO_{4+\delta}$, and $LaNiO_3$. Above 100–150 K, the thin films have a temperature independent dielectric constant as do crystals. The value of the dielectric constant is of the order of 1500 over a wide temperature region, potentially making it a good candidate for many applications. The frequency dependence of its dielectric properties below 100–150 K indicates an activated relaxation process. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1506951]

Ferroelectric or relaxor materials, such as $(Ba,Sr)TiO_3$,[1] $SrTiO_3$ (STO),[2] and $KTa_{1-x}Nb_xO_3$,[3] have been widely studied for various electronics applications, including dynamic random access memory. This is because, in general, a high static dielectric constant is only observed in either a ferroelectric or a relaxor material. However, both types of material show a peak in the dielectric constant as a function of temperature, making it undesirable for many applications because a strong temperature dependence may cause the related device to fail with temperature variations in the environment. Recently, $CaCu_3Ti_4O_{12}$ (CCTO) was discovered to have an extraordinarily high dielectric constant ~80 000 at room temperature with minimal temperature dependence above 100 K.[4–6] No ferroelectric lattice distortion has been observed by either high-resolution x-ray[5] or neutron powder diffraction,[4] posing interesting questions: Why does the material have such a giant dielectric constant and why does the latter decrease dramatically below 100 K. It is therefore of considerable interest both from a fundamental and an application point of view to see whether one can make thin films of this material and examine its properties. In this letter, we show that high-quality CCTO thin films can be epitaxially grown on various substrates with or without conducting buffer layers. The low-frequency dielectric constant is lower than that of the crystal, but still ~1500 over a wide temperature region, making it a competitive candidate for many applications.

The CCTO thin films were grown by pulsed-laser deposition (PLD) on $LaAlO_3$ (LAO) or STO substrates, as well as $YBa_2Cu_3O_7$ (YBCO), $La_{1.85}Sr_{0.15}CuO_{4+\delta}$ (LSCO), and $LaNiO_3$ (LNO) buffer electrode layers. These electrode layers were also deposited on the substrates *in situ* by PLD before the deposition of the CCTO thin film. The CCTO target was prepared by solid-state reaction with the purity of the powders confirmed by x-ray powder diffraction. A KrF excimer laser (wavelength: 248 nm) was used with an energy density of ~2.0 J/cm^2 and a repetition rate of 5 Hz. The substrate was heated to 720 °C (800 °C for the YBCO layer). An oxygen pressure of 200 mTorr was used during the deposition for all materials. After deposition, the films were cooled to room temperature at a rate of 60 °C per minute. Au pads, 0.5 mm^2 in area with a thickness of about 4000 Å, were thermally evaporated to form a parallel-plate capacitor structure. Due to the difficulty of etching the CCTO thin films while maintaining the film quality, contacts were made to two of the top Au pads effectively, allowing the capacitance to be measured in two capacitors connected in series by the bottom electrodes. Dielectric constants and loss tangents were measured by a Keithley 3330 LCZ meter from 200 Hz to 100 kHz.

Thin films grown directly on STO substrates do not have the correct phase or may have more than one orientation of CCTO. This is understandable since the lattice mismatch between STO and CCTO is large. CCTO has a cubic structure with a lattice constant $a=7.36$ Å ($a/2=3.68$ Å), while STO has a cubic lattice constant $a=3.905$ Å. Thin films grown on the LAO substrate have only one orientation. This is shown in Fig. 1(a) in a θ–2θ x-ray diffraction scan. Only the $(\ell 00)$ peaks from CCTO are present indicating that the out-of-plane alignment is good. The substrate temperature and the oxygen pressure were found to be crucial for single-phase formation of CCTO. Indeed, thin films deposited at 780 °C or 20 mTorr were found to include the (310) orientation. In order to make dielectric measurements, various conducting perovskite oxides were fabricated as the bottom electrodes. Shown in Fig. 1(b) is a θ–2θ scan of a 6000 Å CCTO thin film on a 1500 Å LSCO buffer layer on the STO substrate. Only the (00ℓ) peaks from both CCTO and LSCO layers are

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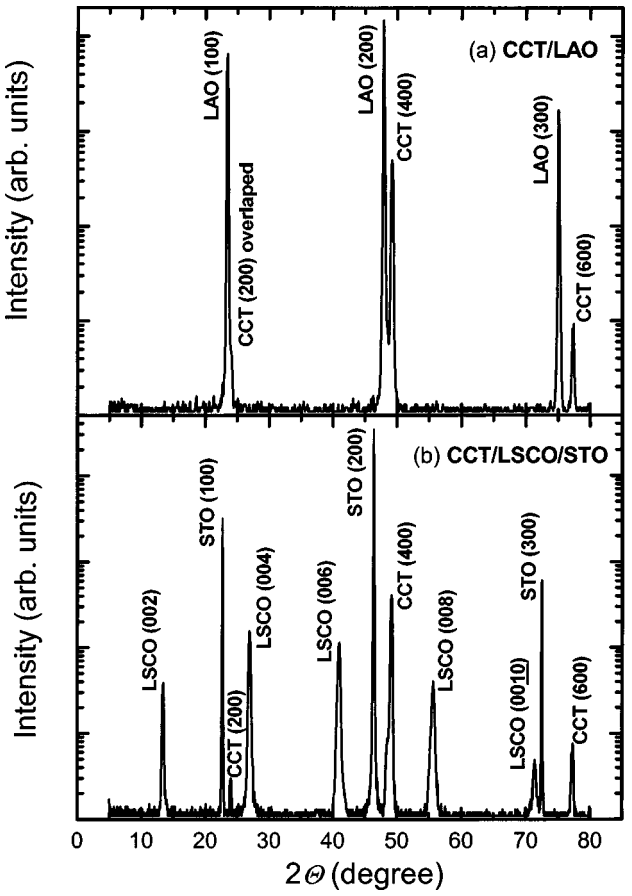

FIG. 1. θ–2θ scan of (a) a 6000 Å CCTO thin film on LAO substrate and (b) a 6000 Å CCTO thin film on a 1500 Å LSCO electrode layer on STO substrate.

present in the spectrum with peaks from the STO substrate, indicating both layers grow with the *c* axis perpendicular to the substrate surface. It is worth pointing out that, with a LSCO buffer layer, the CCTO thin films can also be grown epitaxially on a STO substrate.

The in-plane epitaxy of the CCTO thin films were examined by ϕ scans. Figure 2 shows the results of such a scan from the same bilayer thin film as in Fig. 1(b). Sharp peaks appear with 90° intervals for both the CCTO and LSCO layers, and the STO substrate, indicating the *a* axis of the CCTO and LSCO layers are well aligned with the substrate. Combined with the θ–2θ scan, it shows we have an excellent epitaxy between the CCTO thin film, the LSCO buffer layer and the STO substrate. Thus, we are in a position to study the properties of CCTO in thin-film format.

Because LNO has a lattice constant closer to CCTO than YBCO and a much better conductivity than LSCO, we made our measurement on thin films of CCTO/LNO/LAO. The temperature dependence of the dielectric constant and loss tangent for such a film at various frequencies from 200 Hz to 100 kHz is shown in Figs. 3(a) and 3(b), respectively. The dielectric constant has a fairly high value at room temperature, but, unlike the crystal data, with a large frequency dependence. It decreases rapidly with decreasing temperature. The loss tangent shows the same trend with temperature. In fact, both are very similar to the very first report by Subramanian *et al.*[4] at a high temperature. Below a temperature of 250 K, the film behaves almost exactly the same as a crystal.

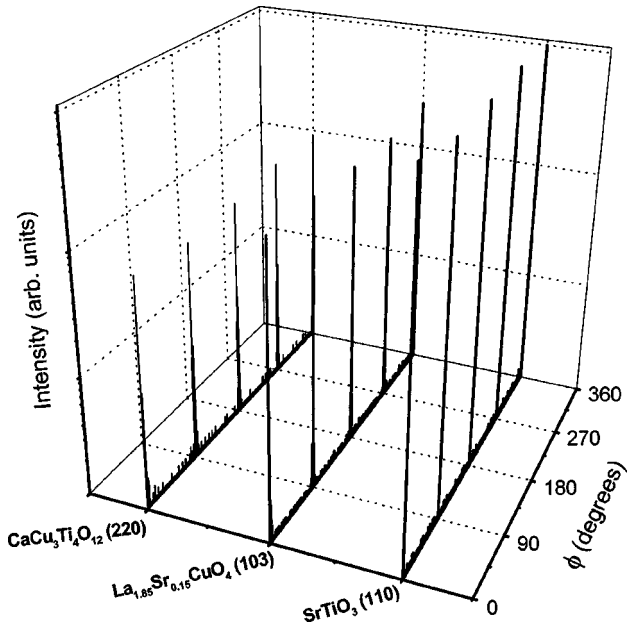

FIG. 2. ϕ scan of the (220) peak from CCTO thin film and (103) peak from LSCO buffer layer. This is a 6000 Å CCTO/1500 Å LSCO bilayer thin film on STO substrate.

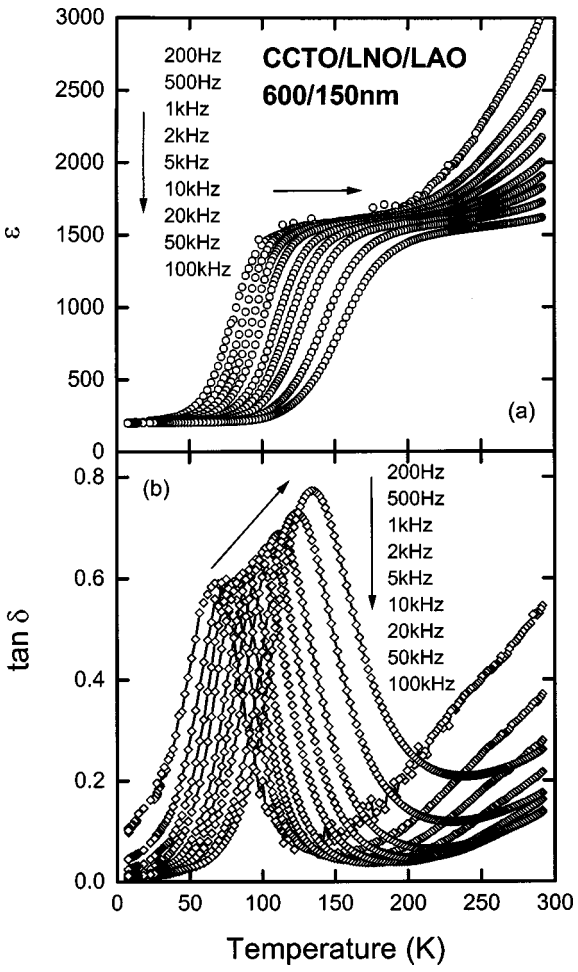

FIG. 3. Temperature dependence of (a) the dielectric constant and (b) the loss tangent tan δ of a 6000 Å CCTO thin film grown on LNO electrode layer on LAO substrate from 200 Hz to 100 kHz.

The dielectric constants at all frequencies have a constant value of the order of 1500 until about 100–150 K, when they decrease rapidly to approximately 200. This value is different from that of the crystal, which is about 100.[6] Obviously, the system undergoes a transition from a high ϵ state at a high temperature to a low ϵ state at a low temperature, and the frequency dependence only takes place around the transition temperature regime, which is about 100–150 K. The transition takes place at higher temperatures at higher frequencies. Correspondingly, the peak observed in the temperature dependence of the loss tangent, shifts toward a higher temperature. Finally, it is interesting to note that the results shown in Fig. 3 are very similar to those from the bulk material $CdCu_3Ti_4O_{12}$, which does not have the same giant dielectric constant at room temperature as bulk CCTO.[7]

The large dielectric constant of CCTO has been interpreted as an extrinsic mechanism, which was assumed to come from the sample microstructure such as boundary or interface effects.[8] In fact, one recent paper has claimed that CCTO is a one-step internal barrier layer capacitor.[9] With such a model, one would conclude that the thin films have less defects than the crystals because of their lower dielectric constant. This is a possibility though it can often be the reverse. Thin films, with their much reduced size in one dimension, may have less planar defects, such as grain boundaries and twin interfaces, than crystals, particularly if the latter have a large amount of intrinsic planar defects. Comparing the data from the crystals and the thin films, it seems that the constant value of the dielectric constant in a certain temperature region and the decrease at a low temperature is a consistent property of the material, presenting an interesting problem as to why the dramatic increase at even a higher temperature only shows up in thin films or polycrystalline samples.[4] The dielectric constant also has a significant dependence on the thickness of the CCTO thin films. To date, thin films with a thickness less than 3000 Å have a much lower dielectric constant ($\sim$700). Growth conditions, such as oxygen pressure, cooling rate, or different conducting bottom electrode layer, are still to be optimized. These studies, as well as the thickness dependence of the dielectric properties, will be published elsewhere.

Finally, it is worth pointing out that the loss tangent in the thin film is actually lower than in the crystal. This may well be a reflection that the crystals have more defects than the thin films. Since the low-temperature decrease of the dielectric constant toward 100 or 200 is certainly associated with the peak observed in the temperature dependence of the loss tangent, this might just be due to the fact that the constant value ($\sim$1500) of the dielectric constant in the thin film is much lower than in the crystal ($>$10 000). A precise description should involve an understanding of the observed peak. Homes *et al.*[6] used a Debye relaxation model to describe the frequency dependence of the dielectric constant and find a thermally activated behavior with an activation energy of about 630 K in crystal. Here, we show a simple way to get a similar result from our loss tangent data. In Fig. 4, we plotted the frequency on a logarithmic scale versus the inverse peak temperature in our loss measurement. Along with the thin-film data we also show the data from a crystal. Clearly, a linear dependence is observed, indicating that

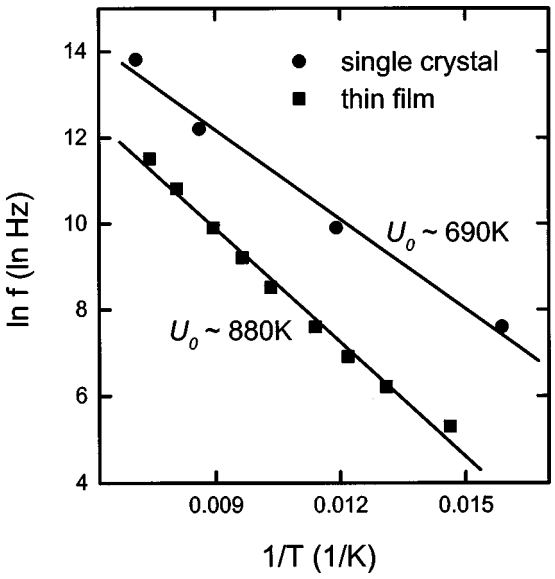

FIG. 4. The log of the frequency versus inverse peak temperature in loss measurement. Both the data from thin film and crystal are presented. A thermally activated behavior $f \sim \exp(-U_0/kT)$ is clearly observed.

$f \sim \exp(-U_0/kT)$, in both sets of data. U_0 for the crystal is 690 K which is about the same as the value from fitting to the Debye relaxation model for the dielectric constant.[6] U_0 for the thin film is 880 K. The difference may well reflect the fact that the thin film is under strain due to the lattice mismatch. Of course, the microstructure, defects, and domain difference would also play a role. Further study on the evolution of the activated relaxation with thin-film thickness will be conducted.

In conclusion, we have grown epitaxial CCTO thin films by PLD. Thin films have similar properties to the previously studied crystals at low temperature. The dielectric constant is above 1500 within a fairly large temperature region, making it a very attractive material for many applications. Further investigations including the thickness dependence and electric-field dependence are underway.

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